

# Emergence of correlated proton tunneling in water ice

Onur Pusuluk,<sup>1</sup> Tristan Farrow,<sup>2,3</sup> Cemsinan Deliduman,<sup>4</sup> and Vlatko Vedral<sup>2,3</sup>

<sup>1</sup>*Department of Physics, İstanbul Technical University, Maslak, İstanbul, 34469 Turkey*

<sup>2</sup>*Department of Physics, University of Oxford, Parks Road, Oxford, OX1 3PU, UK*

<sup>3</sup>*Centre for Quantum Technologies, National University of Singapore, 3 Science Drive 2, Singapore 117543, Singapore*

<sup>4</sup>*Department of Physics, Mimar Sinan Fine Arts University, Bomonti, İstanbul, 34380, Turkey*

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Several experimental and theoretical studies report instances of concerted or correlated multiple proton tunneling in solid phases of water. Here, we construct a pseudo-spin model for the quantum motion of protons in a hexameric H<sub>2</sub>O ring and extend it to open system dynamics that takes environmental effects into account. We approach the problem of correlations in tunneling using quantum information theory in a departure from previous studies. Our results show that one of the principal measures of coherence,  $l_1$  norm of coherence, is sufficient to capture the behaviour of coherent proton mobility observed in experiments. We conclude that individual quantum tunneling events are classically rather than quantum correlated at low temperatures.

Hydrogen bonding (or H-bonding) is the subject of extensive literature due to its central importance in many natural phenomena in physical, chemical, and biological systems. The first attempts that reveal the underlying physics behind it go back to the 1950s [1, 2], and since then, quantum aspects of the nature of this weak interaction are still being hotly debated. In the meantime, most of the demystification attempts have focused on the H-bonds using water as an explanatory model [3–6].

Let's designate a H-bonded system  $X_1-H \cdots X_2$  where the single covalent bond  $X_1-H$  is a proton-donating bond,  $X_1$  is the proton-donor and  $X_2$  is the proton-acceptor. One controversial issue about the role of non-trivial quantum effects in such a system is the extent of the covalency of the  $H \cdots X_2$  interaction [3], i.e. charge transfer from the lone pair orbital of the proton-acceptor ( $\sigma_{LP(X_2)}$ ) to the unoccupied antibonding orbital of the proton-donating bond ( $\sigma_{X_1-H}^*$ ). Although the covalent contribution to the attractive energy of H-bonds in water is comparable to the electrostatic contribution, the amount of charge transfer itself is of the order of just a few millielectrons [4].

Apart from this intermolecular charge transfer, non-trivial quantum effects also enter into the physics of H-bonding in the form of proton tunneling back and forth between donor and acceptor. According to diabatic state models [5, 6], nuclei of H atoms are likely to tunnel through H-bonds between water monomers. Several *ab initio* studies examined this probability in water ice as well. First and foremost, proton tunneling was found to be responsible for the pressure driven phase transitions from proton-ordered ice VIII to proton-disordered ice VII around 100 K [7], and is believed to drive the transition from proton-disordered ice I<sub>h</sub> to proton-ordered ice XI in a microscopic model [8].

However, spontaneous single proton tunnelings violate the so-called Bernal-Fowler *ice rules* [9, 10] which state that (i) each water molecule is linked to four other ones through H-bonds in such a way that (ii) it behaves as a

proton-donor in half of these four bonds and a proton-acceptor in the remaining ones. These local constraints are expected to lead to correlations between individual proton tunnelings. Consistent with this expectation, the likelihood of correlated proton tunneling in water ice was recently reported by successive low-temperature experiments such as incoherent quasielastic neutron scattering measurements on ice I<sub>h</sub> and I<sub>c</sub> [11], scanning tunnelling microscopy of cyclic water tetramer [12], and high precision measurements of the complex dielectric constant of ice XI [13]. Proton correlations in ice VII, VIII, and I<sub>h</sub> have been investigated using one-particle density matrix analysis [14] confirming their presence only in ice VII. On the contrary, concerted tunneling of six protons in ice I<sub>h</sub> appeared to occur at low temperatures in path integral simulations [15] and in lattice-based calculations [16].

Here, we introduce a pseudo-spin model for the quantum motion of protons in a hexameric H<sub>2</sub>O ring. Unlike considerations of pseudo-spins by previous studies [8, 16], we do not attempt to impose the six proton tunneling by effectively incorporating a single matrix element into the Hamiltonian, or to map the problem onto a lattice gauge theory. Instead, we develop an extension of the model to open system dynamics and approach the correlation problem from the standpoint of quantum information theory. Temperature dependence of proton correlations in (athermal) equilibrium are monitored by well-known measures of quantumness such as entanglement of formation [17], concurrence [18], quantum discord [19, 20], geometric measure of discord [21], relative entropy of coherence [22], and  $l_1$  norm of coherence [22].

Although their unit cells belong to different space groups, the basic structures of both ice I<sub>h</sub> and XI can be visualized as a hexameric box whose planes are either chair-form or boat-form 3-d hexamers. To reduce the complexity, we restrict our model to a 2-d hexagonal ring with a hydroxyl ion (OH<sup>−</sup>) resides in each vortex, as shown in Fig. 1a. Rigid rotations of the vertices are not taken into account because of the high energy cost.

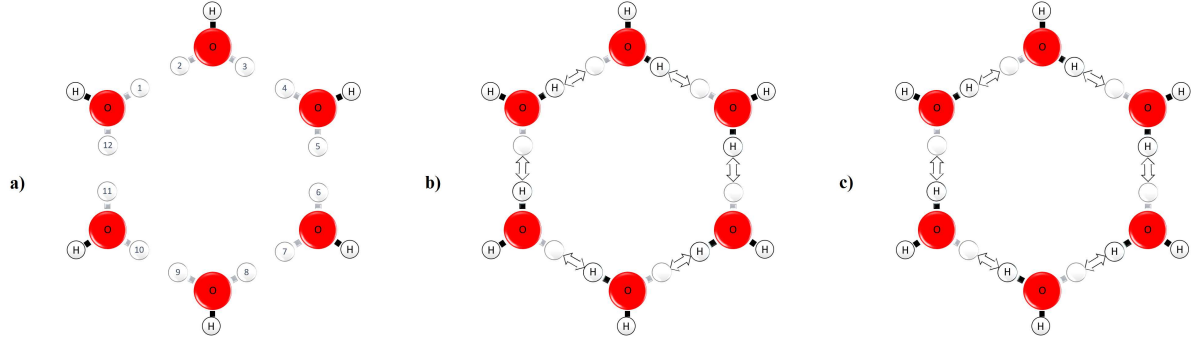


FIG. 1: (a) The hexagonal lattice is made of  $\text{OH}^-$  ions in fixed positions relative to each other. Edges can be interpreted as H-bonds. Protons are allowed to live on the enumerated locations. Ice rules are satisfied only by 2 of the six-proton configurations in (b) and (c). Transitions between them require simultaneous tunneling of the six protons within the ring in the directions depicted by two-sided arrows. Any other configuration accessible from (b) or (c) by individual proton tunneling through H-bonds is called an ionic defect. Bjerrum defects occur in all the other configurations including the remaining six-proton configurations.

Each edge linking two vertices represents a H-bond and includes two equally likely locations for  $\text{H}^+$  ions. These locations (enumerated in Fig. 1a) can be regarded as a crystal lattice in which  $\text{H}^+$  ions, or protons, move according to the Hamiltonian

$$H_{Hex} = \sum_{j=1}^{12} W_j n_j - \sum_{j=1}^{12} J_{j,j+1} (a_j^\dagger a_{j+1} + a_j a_{j+1}^\dagger) + \sum_{j=1}^{12} V_{j,j+1} n_j n_{j+1} + \lambda, \quad (1)$$

where subscripts are in mod 12,  $n_j = a_j^\dagger a_j$  is the proton number operator at lattice site  $j$ ,  $a_j^\dagger$  and  $a_j$  are respectively proton creation and annihilation operators that obey the following anticommutation relations

$$\{a_j, a_k\} = \{a_j^\dagger, a_k^\dagger\} = 0, \{a_j, a_k^\dagger\} = \delta_{jk}. \quad (2)$$

On-site energy  $W_j$  can be taken as the total potential felt by a proton at  $j$ th site, i.e. the sum of a Morse potential describing the single (covalent) bond with the adjacent  $\text{OH}^-$  ion and a Coulomb potential representing the electrostatic attraction to the opposite  $\text{OH}^-$  ion.  $J_{j,j+1}$  stands for the orbital interactions which causes proton tunneling. Its expected dependence on the geometry implies that  $J_{j,j+1}^{(\text{edge})} \gg J_{j,j+1}^{(\text{vortex})}$  where the former is the intermolecular proton tunneling coefficient for the neighbouring sites occupying the same edge, while the latter is the intramolecular proton tunneling coefficient for the successive sites close to the same vortex. As  $J_{j,j+1}^{(\text{edge})}$  should already be quite small compared to other coefficients, we can neglect  $J_{j,j+1}^{(\text{vortex})}$ .  $V_{j,j+1}$  is introduced to penalize two-proton cases associated with the violation of ice rules. Edge sharing sites and vortex sharing sites have different penalty coefficients as well as different tunneling coefficients. Presence of two protons on

the same edge is called as a Bjerrum defect, whereas occupation of both sites near the same vortex is called as an ionic defect. As Bjerrum defects require more energy,  $V_{j,j+1}^{(\text{edge})} \gg V_{j,j+1}^{(\text{vortex})}$ . Finally,  $\lambda$  is a constant responsible for the total intermolecular interactions between vertices, such as Pauli repulsion, Van der Waals interaction, and London dispersion.

Symmetry of the lattice provides that  $W_j = W$ ,  $J_{j,j+1}^{(\text{edge})} = J$ ,  $V_{j,j+1}^{(\text{edge})} = V_{\text{inter}}$ , and  $V_{j,j+1}^{(\text{vortex})} = V_{\text{intra}}$ . To obtain a pseudo-spin Hamiltonian by preserving the anti-commutation relations (given in Eq. (2)), we apply the Jordan-Wigner transformation for  $a_j$ ,  $a_j^\dagger$ , and  $n_j$  in Eq. (1) in such a way below

$$\begin{aligned} a_j &= \exp \left( -i\pi \sum_{k=1}^{j-1} \sigma_-^{(k)} \sigma_+^{(k)} \right) \sigma_+^{(j)}, \\ a_j^\dagger &= \exp \left( +i\pi \sum_{k=1}^{j-1} \sigma_-^{(k)} \sigma_+^{(k)} \right) \sigma_-^{(j)}, \\ n_j &= \sigma_-^{(j)} \sigma_+^{(j)}, \end{aligned} \quad (3)$$

where  $\sigma_-^{(j)} = |1_j\rangle\langle 0_j|$  and  $\sigma_+^{(j)} = |0_j\rangle\langle 1_j|$  with the convention for Pauli  $z$  operator that  $\sigma_z^{(j)} = |0_j\rangle\langle 0_j| - |1_j\rangle\langle 1_j|$ . Note that in contrast to the standard application of the Jordan-Wigner transformation on electron transport phenomena, the creation of a proton at the  $j$ th site is an energy lowering process here.

After writing (3) in terms of Pauli operators, i.e.  $n_j = \frac{1}{2} (I^{(j)} - \sigma_z^{(j)})$  and  $\sigma_\pm^{(j)} = \frac{1}{2} (\sigma_x^{(j)} \pm i\sigma_y^{(j)})$ , we substitute it into (1) and arrive at the following pseudo-spin

Hamiltonian

$$\begin{aligned}
H_{Hex} = & - \sum_{j=1}^6 J_x \left( \sigma_x^{(2j-1)} \otimes \sigma_x^{(2j)} + \sigma_y^{(2j-1)} \otimes \sigma_y^{(2j)} \right) \\
& + \sum_{j=1}^6 J_z^{(\text{inter})} \left( \sigma_z^{(2j-1)} \otimes \sigma_z^{(2j)} \right) \\
& + \sum_{j=1}^6 J_z^{(\text{intra})} \left( \sigma_z^{(2j)} \otimes \sigma_z^{(2j+1)} \right) \\
& + \sum_{j=1}^{12} B \sigma_z^{(j)} + \tilde{\lambda},
\end{aligned} \tag{4}$$

where the superscripts of the Pauli matrices are in mod 12,  $J_x = J/2$ ,  $J_z^{(\text{inter})} = V_{\text{inter}}/4$ ,  $J_z^{(\text{intra})} = V_{\text{intra}}/4$ ,  $B = -(2W + V_{\text{inter}} + V_{\text{intra}})/4$ , and  $\tilde{\lambda} = \lambda + 6W + 3(V_{\text{inter}} + V_{\text{intra}})/2$ .

It is hard to draw a generic model of the environment for the motion of protons through H-bonds. Such a model should include at least three kinds of vibrations as each individual H-bond is defined by three geometric parameters, e.g. length of the proton-donating bond, donor-acceptor separation and bond angle. In a realistic H-bonded complex, the solvent has also a significant effect on the open system dynamics, and the environment of biological H-bonds becomes more elaborate due to the presence of a surrounding protein. However, a minimalistic model consisting of just the periodic oscillations associated with the lengths of proton-donating bonds seems to be sufficient to describe the low-temperature dynamics of protons in a hexameric H<sub>2</sub>O ring. These oscillations can be incorporated into our model as independent thermal baths around lattice sites with individual self-Hamiltonians

$$H_B^{(j)} = \sum_k \hbar \omega_{j,k} b_{j,k}^\dagger b_{j,k}, \tag{5}$$

where  $b_{j,k}^\dagger$  and  $b_{j,k}$  are phonon creation and annihilation operators associated with the  $k$ th oscillator mode at the  $j$ th site. We assume that the positions of the protons are linearly coupled to the equilibrium positions of the phonons through

$$\begin{aligned}
H_I = & \sum_j n_j \sum_k \left( g_{j,k} b_{j,k}^\dagger + g_{j,k}^* b_{j,k} \right) \\
& \propto \sum_j \sigma_z^{(j)} \sum_k \left( g_{j,k} b_{j,k}^\dagger + g_{j,k}^* b_{j,k} \right).
\end{aligned} \tag{6}$$

It is important to realize that the local interaction described above induces the entanglement of each pseudo-spin state with the positions of associated phonons. In the absence of spin-spin coupling ( $J_x = 0$ ), the dynamics of the pseudo-spin states are fully separated from each other, and each pseudo-spin undergoes a pure dephasing process.

Before extending this discussion to the case of non-vanishing inter-spin coupling, let us first examine the role of memory effects in open system dynamics. The Born-Markov approximation can be justified only if the state of pseudo-spins varies over a time scale much longer than the lifetime of the environmental excitations. The excitation of O–H bond in heavy ice I<sub>h</sub> decays over a time just below 0.4 ps [23], while the lifetime of a O–D stretch vibration in light ice I<sub>h</sub> is around 0.48 ps up to 80 K [24]. Unlike the short-lived H-bonds in liquid water [25], H-bonds survive sufficiently long in ice I<sub>h</sub>, and so, we can describe (supra-)picosecond evolution of the pseudo-spin states on the basis of a Markovian master equation in the following Lindblad form [26]

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H_{Hex} + \hbar H_{LS}, \rho] + \mathcal{D}(\rho), \tag{7}$$

where the Lamb shift Hamiltonian provides a unitary contribution to the open dynamics and reads

$$H_{LS} = \sum_{\omega} \sum_{j,j'} S_{jj'}(\omega) A_j^\dagger(\omega) A_{j'}(\omega), \tag{8}$$

whereas the dissipator is defined by

$$\begin{aligned}
\mathcal{D}(\rho) = & \sum_{\omega} \sum_{j,j'} \gamma_{jj'}(\omega) (A_{j'}(\omega) \rho A_j^\dagger(\omega) \\
& - \frac{1}{2} \{A_j^\dagger(\omega) A_{j'}(\omega), \rho\}),
\end{aligned} \tag{9}$$

with  $\omega = \epsilon_m - \epsilon_{m'}$ . Here,  $\epsilon_m$ 's are the eigenvalues of pseudo-spin Hamiltonian given in (4) and Noise operators  $A_j(\omega)$  are the eigenoperators of this self-Hamiltonian

$$A_j(\omega) = \sum_{\epsilon_m - \epsilon_{m'} = \omega} |\epsilon_{m'}\rangle \langle \epsilon_{m'} | A_\alpha | \epsilon_m \rangle \langle \epsilon_m|, \tag{10}$$

where  $A_j$  are the Hermitian operators coupled to the environment, i.e. Pauli  $z$  operators as introduced in Eq. (6). Coefficients  $S_{jj'}(\omega)$  and  $\gamma_{jj'}(\omega)$  are respectively the imaginary part and half of the real part of the one-sided Fourier transformation of the thermal bath correlation function given by

$$\Gamma_{jj'}(\omega) = \frac{1}{\hbar^2} \int_0^\infty ds e^{i\omega s} \langle B_j^\dagger(s) B_{j'}(0) \rangle_{\text{th}}, \tag{11}$$

where  $B_j(s)$  are the interaction picture representations of the bath operators (included in (6)) and  $J(\omega)$  is the spectral density function encapsulating all the effects of the environment. We can assume  $\Gamma_{jj'} = \Gamma_{jj}$  because each pseudo-spin is associated to an independent environment. Furthermore, since we focus on a symmetric lattice at a constant temperature  $T$ , these individual baths are identical and we can get  $\Gamma_{jj} = \Gamma$ .

Here and in the following, we consider the steady state solution of the Eq. (7). Interaction with the environment

does not bring the system into a thermal equilibrium in general. On the contrary, it divides  $2^{12}$ -dimensional Hilbert space  $\mathcal{H}$  into subspaces  $\mathcal{H}_{\mathcal{J}}$  each of which is independently invariant under  $\{A_j\}_{j=1}^{12}$  operators. In the asymptotic limit, it provides a detailed balance only inside these subspaces as below:

$$\rho_{\infty} = \sum_{\mathcal{J}} \frac{P(\mathcal{J})}{Z(\mathcal{J})} \sum_{|\epsilon_m\rangle \in \mathcal{H}_{\mathcal{J}}} e^{-\beta \epsilon_m} |\epsilon_m\rangle \langle \epsilon_m|, \quad (12)$$

where

$$P(\mathcal{J}) = \sum_{|\epsilon_m\rangle \in \mathcal{H}_{\mathcal{J}}} \langle \epsilon_m | \rho(t=0) | \epsilon_m \rangle, \quad (13)$$

and

$$Z(\mathcal{J}) = \sum_{|\epsilon_m\rangle \in \mathcal{H}_{\mathcal{J}}} e^{-\beta \epsilon_m}, \quad (14)$$

with  $\beta = 1/k_B T$ .

Both of the ice  $I_h$  and XI obey the ice rules. However hexagonal rings of ice XI possess a global proton order which is absent in ice  $I_h$ , i.e.  $H_2O$  hexamers sharing the same 3-d form and the same orientation have also the same proton configuration. This proton order can't be preserved in the presence of proton tunneling unless each of these hexamers simultaneously switches into another proton configuration through collective six-proton tunneling. In our model,  $|01\rangle^{\otimes 6}$  and  $|10\rangle^{\otimes 6}$  pseudo-spin states (respectively depicted in Fig. 1b and c) are similar to these two configurations. They span the whole subspace in which the single hexamer satisfies the ice rules. If we extended our model by connecting multiple hexamers in 3-d, the tensor product of these subspaces could indeed correspond to proton-ordered phase. Also, the subspace spanned by ionic defects in our model could come together and incorporate into the ice rule preserving subspace in such an extended Hilbert space. This additional part of the ice rule preserving subspace would coincide with the proton-disordered phase.

In this respect, although this study focuses on a single hexamer, we will treat 2 pseudo-spin states obeying ice rules as proton-ordered phase and 62 pseudo-spin states corresponding to ionic defects as proton-disordered phase. Actually, one of the subspaces  $\mathcal{H}_{\mathcal{J}}$  mentioned in the previous section is constituted by these two kinds of pseudo-spin states. If the initial state  $\rho(t=0)$  lives only in this 64-dimensional subspace,  $\mathcal{H}_{ice}$ , the state of the pseudo-spins that relax to equilibrium still stays inside the same subspace as follows

$$\rho_{\infty}^{ice} = \sum_{|\epsilon_m\rangle \in \mathcal{H}_{ice}} e^{-\beta \epsilon_m} |\epsilon_m\rangle \langle \epsilon_m| / \sum_{|\epsilon_m\rangle \in \mathcal{H}_{ice}} e^{-\beta \epsilon_m}. \quad (15)$$

It is straightforward to show that the athermal attractor above essentially depends two free parameters,  $J_x$  and

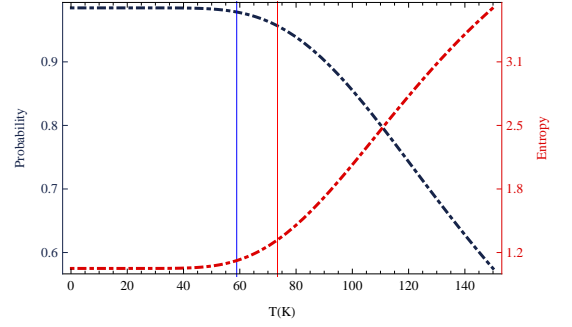


FIG. 2: XI $\rightarrow$ I $_h$  and I $_h\rightarrow$ XI phase transitions of hexagonal ice respectively occur at 58.9 K and 73.4 K [29]. Vertical solid lines coloured blue and red pinpoint these temperatures. The dashed dark blue curve is the probability of pseudo-spins to be found inside the ice rule preserving subspace spanned by  $\{|01\rangle^{\otimes 6}, |10\rangle^{\otimes 6}\}$ . We set  $J_x$  and  $J_z^{(intra)}$  respectively to  $-1$  meV and  $+10$  meV to observe the violation of ice rules around the phase transition temperatures. The dashed dark red curve shows the temperature dependence of the von Neumann entropy.

$J_z^{(intra)}$  as all the energy eigenvalues of subspace  $\mathcal{H}_{ice}$  have a common functional dependence on the remaining coefficients included in (4). The values of the parameters used here were estimated from comparisons of the predictions of the model with the previous experiments carried out on the ice  $I_h$ /XI transition. Actually, it isn't easy to observe this transition as protons are expected to become classically immobile around 100 – 110 K where a glass transformation occurs [27–29]. First calorimetric measurements [30, 31] overcame this problem by using alkali hydroxides as catalyzer and caught the transition at 72 K. According to recent complex dielectric constant measurements of pure water ice reported in [29], hexagonal ice undergoes a phase transition from proton-disordered ice  $I_h$  to proton-ordered ice XI at 58.9 K, whereas a reverse transformation occurs at 73.4 K. Thus, we fixed the free parameters to reproduce a similar trend in the total probability of pseudo-spins being in a state  $|01\rangle^{\otimes 6}$  or  $|10\rangle^{\otimes 6}$  as shown in Fig. 2. Values of  $J_x = -1$  meV and  $J_z^{(intra)} = +10$  meV found in this way are expectedly much smaller than the energy of a H-bond.

To provide a first insight into the quantum aspects of the proton mobility in a hexameric  $H_2O$  loop, we apply two well-known coherence based measures of quantum correlations on  $\rho_{\infty}^{ice}$ . The first measure is  $l_1$  norm, which is simply defined as  $\sum_{m \neq m'} |(\rho)_{jk}|$ . It quantifies the quantum coherent proton mobility as non-diagonal elements of  $\rho_{\infty}^{ice}$  represent the transition probabilities between pseudo-spin states, and each pseudo-spin state corresponds to a different configuration of six protons. On the other hand, the relative entropy of coherence measures the distinguishability of a density matrix with a modified copy in which diagonal elements are removed.

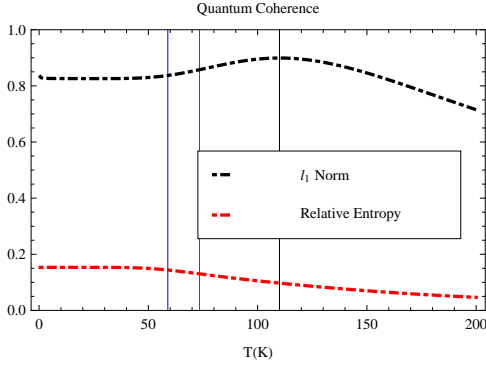


FIG. 3: Coherent quantum effects on proton mobility in a H<sub>2</sub>O hexamer. Vertical solid lines coloured blue and red indicate the phase transition temperatures [29], whereas the vertical black line is anchored to the temperature of the glass transition at which proton mobility is expected to diminish [27–29].

Thus, it highlights the population probabilities rather than the proton mobility.

Quantum coherent proton mobility shows a local minimum below 50 K in Fig. 3. Although the resolution is not suitable to work out the exact location of the minimum, this observation seems to be in accordance with the dielectric anomaly measured in the form of a minimum around 20 K [13]. When we consider Fig. 2 as well, we can gain a deeper understanding of this experimental finding where we suspect a concerted quantum tunneling of six protons could be occurring in each hexamer. As well as the entropy of the system, its probability of obeying ice rules is also around 1 below 50 K. Thus, the state of the pseudo-spins should be a maximal mixture of two states, such as  $\{P = 1/2, (|01\rangle \otimes^6 + |10\rangle \otimes^6) / \sqrt{2}; P = 1/2, (|01\rangle \otimes^6 - |10\rangle \otimes^6) / \sqrt{2}\}$ . Each of the symmetric and antisymmetric superposition states involved in this mixture can be interpreted as a concerted tunneling of six protons back and forth between the states  $|01\rangle \otimes^6$  and  $|10\rangle \otimes^6$ .

Protons are expected to become classically immobile around 100 – 110 K where a glass transformation occurs [27–29]. Thus, proton tunneling was also claimed to be in charge during the phase transition from proton-disordered ice I<sub>h</sub> to proton-ordered ice XI in a previous study based on lattice gauge theory [8]. Temperature dependence of  $l_1$  norm in between 60 – 110 K supports the claimed importance of coherent proton mobility on the proton ordering dynamics. It starts to increase with XI→I<sub>h</sub> phase transition and reaches a peak around glass transition.

Now, we will elaborate the underlying mechanism behind the emergence of a correlation between individual proton tunnelings at low temperatures. To do so, let's focus on the correlations between pseudo-spin pairs shown in Figs 4 and -5. Only classical correlations appear be-

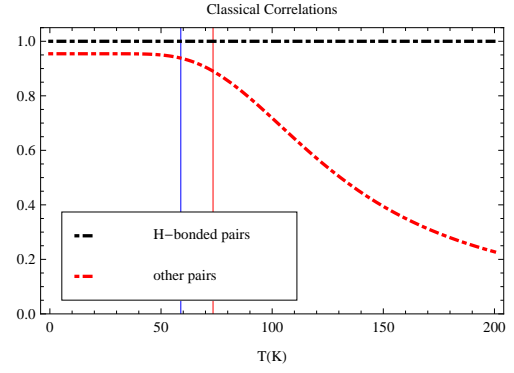


FIG. 4: Pairwise classical correlations. The dashed black curve corresponds to the correlations in a single H-bond. Correlations between two protons, each of which belongs to a different H-bond, is shown by the dashed dark red curve. For the vertical solid lines, see the previous Figs 2 and -3.

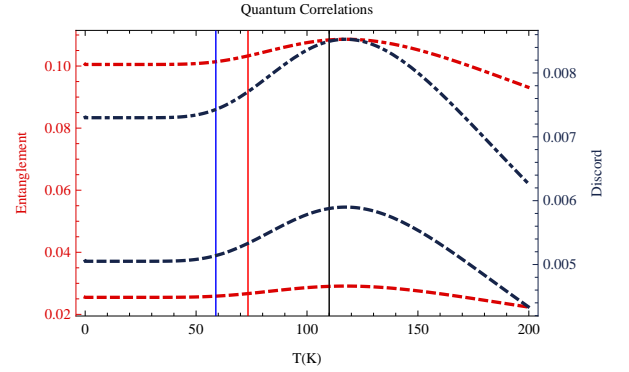


FIG. 5: Pairwise quantum correlations in a single H-bond. There is no quantum correlation found between proton pairs belonging to different H-bonds. The dot-dashed dark red curve is the concurrence between pseudo-spins lying on the same edge, while the dashed red curve is the entanglement of formation between them. Their quantum correlations beyond entanglement are measured by quantum discord and its geometric measure, which are displayed respectively as dot-dashed and dashed dark blue curves. For the vertical solid lines, see the previous Figs 2 and -3.

tween the pseudo-spins lying on different edges, while temperature dependent behaviour of these correlations resembles the probability change observed in Fig. 2. On the other hand, classical correlations between edge sharing pseudo-spins seem to be temperature independent, while the quantum correlations between these pairs show similarity with coherent proton dynamics described by  $l_1$  norm in Fig. 3. Based on these observations, we surmise that all the individual proton tunnelings throughout six H-bonds become classically correlated at low temperatures. These correlations start to weaken during the phase transition from proton-ordered phase to proton-disordered phase. At the same time, quantum

correlations between H-bonded atoms become stronger, reaching a maximum during the glass transition around 110 – 120 K.

The possibility of concerted six-proton tunneling in a hexameric H<sub>2</sub>O ring was investigated using a pseudo-spin model. This tunneling process emerged naturally in the low-temperature dynamics of the open system. Phonon-assistance was found to be central in driving the concerted proton tunneling up to the temperature of the phase transition from ice XI to ice I<sub>h</sub>. Moreover, it was found to be responsible for the emergence of ice rules governing the arrangement of atoms in water ice.

Remaining within the framework of the pseudo-spin model enabled us to approach the correlation problem using the tools of quantum information theory. In turn, we inferred that the  $l_1$  norm of coherence [22] is sufficient to capture the behaviour of coherent proton mobility observed in experiments [13, 29]. It was found that the correlations between six proton tunneling events are not inherently quantum in character. Instead, low rates were observed for quantum tunneling events through individual H-bonds that are strongly correlated below a critical temperature corresponding to phase transition. Beyond this critical temperature, simulations showed a weakening in classical correlations between proton tunneling events, but a strengthening in quantum correlations between H-bonded molecule pairs. Overall this induces a total increment in the coherent proton mobility until achieving a full proton disorder.

The finding enables us to discriminate between quantum and classical correlations in concerted proton tunneling observed in several experimental and theoretical studies.

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